RSC Advances

PAPER



Cite this: RSC Adv., 2014, 4, 57071

Received 18th August 2014 Accepted 27th October 2014 DOI: 10.1039/c4ra08849b

www.rsc.org/advances

1. Introduction

Catalytic dehydrogenation of isobutane over Cobased catalysts[†]

Guowei Wang,^a Xiaolin Zhu,^{ab} Jiaoyu Zhang,^a Yanan Sun,^a Chunyi Li^{*a} and Honghong Shan^a

In this work, to optimize the catalytic performance of Co-based catalysts for isobutane dehydrogenation, the effects of support, calcination temperature and some promoters were investigated systematically. Results of activity tests and catalyst characterization jointly indicated that both the support and calcination temperature influenced Co dispersion, catalyst acid properties and the interaction between support and Co species significantly. Consequently, the adsorption–desorption behaviors for isobutane and isobutene as well as the dehydrogenation performance were further affected. Sulfided Co/SiO₂, with no acidity, exhibited the best performance. Although high calcination temperature was beneficial for achieving a high selectivity to isobutene over Al_2O_3 and $MgAl_2O_4$ supported Co-based catalysts, the inevitable formation of Co_2SiO_4 over Co/SiO_2 at high temperature led to reduced active sites and dehydrogenation activity. In addition, by comparing the different effects of the separate introduction of S, Sn, Cu and Cl, it was concluded that an efficient promoter should present the following characteristics: inhibition of the formation of metal ensembles, and strong binding affinity to two hydrogen atoms of one additive atom.

Lately, dehydrogenation of light alkanes has received great attention as a route to produce the corresponding alkenes, which constitute an important and versatile class of chemical intermediate. However, due to the high cost of platinum and adverse environment effects of chromia,¹ the application of industrialized Pt and Cr_2O_3 -based catalysts has been limited to some extent.

Although high catalytic activity can be obtained over metal (such as Fe, Co and Ni) based catalysts for the conversion of isobutane, the reaction is suffered from an extremely poor selectivity because of aggravated hydrogenolysis reaction, of which the main product is methane rather than isobutene.^{2,3} To address this issue, sulfur was introduced into metal based catalysts in spite that it is usually regarded as an impurity.⁴⁻⁶ Fortunately, we have found that a series of metal sulfide catalysts, either prepared by impregnation with sulfate⁷⁻⁹ or sulfidation with H₂S,^{3,10} exhibit excellent performance in alkane dehydrogenation. The conversion of isobutane over a series of sulfide catalysts of Fe, Co, and Ni reached up to 70 wt%, with a

selectivity to isobutene of around 87 wt%. In general, the promoting effects of introduced sulfur can be understood in two aspects:³ one is a geometric effect to dilute aggregated metallic species and inhibit C–C bond rupture; another is an electronic effect to facilitate olefin desorption and further increase product selectivity. Meanwhile, sulfur loss is speculated to be the origin of catalyst deactivation. To replenish the loss of sulfur, continuous sulfidation-reaction cycles have been carried out and the catalyst performance can be maintained at a high level. Moreover, it should also be noted that, the catalytic performance can be stable for a long period when diluted H_2S is fed together with isobutane.¹⁰

View Article Online

View Journal | View Issue

As mentioned above, the active sites of metal sulfide catalysts and how they interact with isobutane molecules were speculated in our previous study. However, it is still not enough for the preparation of an ideal dehydrogenation catalyst. Firstly, the catalyst support, significantly influencing the dispersion and electronic properties of the active components^{11,12} as well as the acid–base properties of the catalysts,^{13–15} is an important factor to be considered. Meanwhile, some literature reported that high-temperature calcination could modify the catalyst structure and increase the activity and stability of Pd@CeO₂/Si–Al₂O₃ catalyst obviously.¹⁶ Therefore, the effects of both support and calcination condition, directly related to catalyst structure^{16–18} and properties^{19,20} as well as the interaction between active component and support,^{21,22} should be further investigated.

Given the difference in acid-base properties and the interaction with active component, Al_2O_3 , $MgAl_2O_4$ and SiO_2 were

^aState Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China. E-mail: chyli_upc@126.com; chyli@upc.edu.cn; Fax: +86 532 86981718; Tel: +86 532 86981862

^bBeijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra08849b

chosen as the supports of Co-based catalysts separately in this work. Moreover, to examine the effect of calcination temperature, the catalysts with different supports were calcined at both low and high temperatures.

In addition to the support and calcination temperature, the promoter plays a more important role in this catalyst system. As reported in our previous study, metal ensembles catalyze hydrogenolysis reaction to generate methane. Since the hydrogenolysis reaction is structure sensitive,23-27 breaking these metal ensembles and isolating small metal particles seem to be the key in restricting this reaction. To achieve this goal, there are two available methods: reducing metal loading or introducing barriers into the ensembles. As for the former case, although the selectivity to isobutene increased obviously with decreasing metal loading, the catalyst activity decreased sharply,7 indicating the lack of active sites. In contrast, the later approach seems to be more effective: sulfur introduction inhibits the formation of metal ensembles and improves the dehydrogenation performance significantly. Similarly, Apesteguía and Barbier²⁸ also pointed out that presulfidation treatment of Pt-based catalyst could inhibit hydrogenolysis reaction effectively.

Some open literatures reported that the addition of Sn into Pt-based catalyst generated certain geometric and electronic effects, which effectively reduced platinum particles and suppressed coke formation and hydrogenolysis reaction.^{29–32} Similarly, copper addition into nickel-based catalyst also played such a role through the formation of Cu–Ni alloys.^{33,34} In addition, resulting from blockage/electronic effects of the adatom, chlorine modification influenced the adsorptive and catalytic properties of the catalyst remarkably.^{35–37} Therefore, to further explore the promoting mechanism of the additives in this work, Sn, Cu, and Cl have been introduced into Co/SiO₂ catalyst to compare their effects with that of S on the dehydrogenation performance.

2. Experimental

2.1 Catalyst preparation

Alumina was prepared by the sol–gel method. Firstly, pseudoboehmite powder was mixed with distilled water to obtain a suspended solution. After that, HCl solution (36–38 wt%) was added dropwise under vigorous stirring at 70 °C, until a gel-like mixture was formed. To prepare magnesia-alumina spinel, an appropriate amount of magnesium nitrate solution was added into the above gel-like mixture. Then, the mixture was stirred for 2 h, dried at 140 °C for 12 h, and calcined at 700 °C for another 2 h in air. Finally, both gel-like mixtures were crushed and sieved to 80–180 µm for later use. In addition, mesoporous silica (80– 180 µm) was obtained from China Qingdao Haiyang Chemical Company, with a specific surface area of 378.3 m² g⁻¹ and an average pore diameter of 9.6 nm.

Supported catalyst samples were prepared by wetness impregnation of the support with certain amount of cobalt nitrate solution (Co_3O_4 content of the catalyst was 13 wt% in this work). Subsequently, the samples were dried overnight at 140 °C and calcined for 2 h at different temperatures. The as-

prepared samples are denoted as 13Co/support-*x*, where "*x*" indicated the calcination temperature. Moreover, sulfided catalysts were obtained by pretreatment of the samples with H_2S/H_2 (30 mL min⁻¹) for 3 h at 560 °C. Co/SiO₂ catalysts with the introduction of Sn or Cu were prepared by subsequent impregnation of above as-prepared Co/SiO₂ catalysts with ethanol solution of stannous chloride or aqueous solution of copper nitrate, respectively. Cl-modified catalyst was prepared by impregnation of SiO₂ with certain amount of cobalt chloride solution. After the introduction of the promoters, the catalysts were calcined again at 560 °C for 2 h.

2.2 Catalyst characterization

Nitrogen adsorption–desorption measurements were performed on a Quadrasorb SI instrument and a porosimetry analyzer at liquid nitrogen temperature. The specific surface areas and pore volumes of the catalyst samples were determined by the BET and BJH methods. X-ray diffraction (XRD) analysis of the samples was carried out on an X'Pert PRO MPD diffractometer system using Cu K α radiation at 40 kV and 40 mA, running from 5° to 75° with scanning speed at 10° min⁻¹. To determine the content of chlorine on 13Co/SiO₂–Cl catalyst before and after reaction, elemental analysis was carried out by an Axios X-ray flourescence spectrometer (XRF).

Metal dispersion and particle size were determined by H_2 pulse chemisorption using a FINESORB-3010 chemisorption analyzer, with the gas released from the reactor being analyzed by an online GAS-100Q quadrupole mass spectrometer. About 0.3 g of fresh catalyst was reduced *in situ* under a flow of 10 vol% H_2/N_2 (30 mL min⁻¹) at 773 K for 1 h, and then cooled down to 100 °C under the purge of Ar. Afterwards, H_2/N_2 was pulsed into the catalyst bed by the application of a six-way valve until the signal intensity of H_2 did not increase with the pulse number any more. Ultimately, according to the change of area for each pulse, the amount of chemisorbed H_2 was determined, and thus the metal dispersion and particle size can be further calculated.

To investigate the desorption behaviors of the catalysts for alkenes, isobutene desorption test was performed on the same chemisorption analyzer, also equipped with an online MS. For each test, about 0.3 g of sulfided catalyst was loaded into a quartz tube reactor, preheated in a flow of nitrogen (60 mL min^{-1}) at 450 °C for 0.5 h, and then cooled down to 200 °C. Subsequently, with the application of a four-way valve, nitrogen flow was instantaneously switched to a mixture of Ar and isobutene at separate flow rate of 30 mL min⁻¹. After adsorption saturation, the valve was switched back to nitrogen. At that time, the signal for the inert gas decreased immediately since it is hardy adsorbed on catalyst surface. However, the decrease of signal for isobutene was delayed due to its adsorption on the catalyst. Precisely the difference between the signals of inert gas and isobutene gives useful desorption information, for instance, a larger delay extent is indicative of a more difficult isobutene desorption process. Furthermore, such test was also performed at 300 °C and 400 °C.

To compare the adsorption amounts of isobutane or isobutene over different catalysts, pulse chemisorption tests were also carried out using the same equipment with H₂ chemisorption. After pretreatment of 0.3 g of sulfide catalysts in a flow of nitrogen, 0.803 mL of isobutane or isobutene was pulsed into the catalyst bed with a flow of nitrogen (30 mL min⁻¹) at 300 °C. Meanwhile, an online quadrupole mass spectrometer was applied to detect the signals of released hydrocarbons, and the adsorption amount could be further determined by calculating the signal area of each pulse.

The acidic properties of the catalyst samples were determined by temperature-programmed desorption (TPD) of NH₃. For each test, 0.1 g of sample was preheated *in situ* under a helium flow at 600 °C for 0.5 h, and then cooled down to 100 °C. Adsorption was proceeded for 0.5 h under NH₃ flow. Subsequently, the sample was purged under a dry helium flow to remove physically adsorbed NH₃. Ultimately, desorption was initiated at a heating rate of 10 °C min⁻¹ until 600 °C was reached. The amount of desorbed NH₃ was calculated from the area under the TPD curve.

2.3 Catalytic activity test

Catalytic activity tests were performed in a fixed bed microreactor at atmospheric pressure and 560 °C. Prior to reaction, S-modified catalysts were obtained by *in situ* sulfidation with H_2S/H_2 (30 mL min⁻¹) for 3 h at 560 °C, while Sn, Cu, and Clpromoted catalysts were reduced by H_2 (30 mL min⁻¹) for 2 h at 560 °C. During the test, 4 g of catalyst was loaded into the reactor, then a flow of isobutane diluted by nitrogen with a fixed molar ratio of 1 : 6 was fed into the reactor, at a total flow rate of 14 mL min⁻¹. The inner diameter of the reactor is 14 mm, with a length of 160 mm, and the catalyst bed (50 mm long) was loaded between two layers of silica sand. To compare the dehydrogenation performance of different catalysts, the measurements were taken at the initial stage of the reaction. Both the feed and products were analyzed by a Bruker 450 Gas Chromatograph (GC) equipped with an FID detector and two TCD detectors. Furthermore, isobutane dehydrogenation in a pulse mode fixed-bed reactor over Cu-modified catalysts was also conducted. For each test, about 0.1 g of catalyst was loaded and the reaction temperature was maintained at 560 °C. Prior to the reaction, the catalyst was pretreated by a flow of H_2/N_2 (30 mL min⁻¹) for 2 h. Then, pulse feeding was performed using a sixway valve, and 0.803 mL of isobutane was driven into the reactor by nitrogen flow (with a flow rate of 30 mL min⁻¹) in one pulse. Meanwhile, the effluent products were characterized using an online MS, and their mass peaks were registered as follows: H_2 , 2; CH₄, 16; i-C₄H₈, 56 and i-C₄H₁₀, 58.

3. Results and discussion

3.1 Structural characterization and Co dispersion

The XRD patterns of Co-based catalysts supported on the three different supports are illustrated in Fig. 1a. For low-temperature calcined catalysts, diffraction peaks characteristic of both the support and Co_3O_4 were observed. However, with the increase of calcination temperature, some newly emerged diffraction peaks assigned to $CoAl_2O_4$ and Co_2SiO_4 were detected over Co/Al_2O_3 and Co/SiO_2 catalysts, respectively. Meanwhile, the intensities of peaks corresponding to Co_3O_4 decreased to some extent. However, no obvious phase change took place over $Co/MgAl_2O_4$ catalyst with increasing calcination temperature.

Moreover, phase analysis was further carried out over sulfided Co-based catalysts with different supports calcined at both low and high temperatures, and the XRD patterns are shown in Fig. 1b. CoS was present on the surface of catalysts calcined at 560 °C after sulfidation, indicating that sulfidation treatment transformed Co_3O_4 into CoS successfully. However, when the calcination temperature increased to 800 °C, stable CoAl₂O₄ and Co_2SiO_4 , which were difficult to be sulfided, formed on the surface of Co/Al₂O₃ and Co/SiO₂ catalysts, respectively. In addition, compared with low temperature calcined samples, the



Fig. 1 XRD patterns of different Co-based catalysts before (a) and after (b) sulfidation: (1) 13Co/Al₂O₃-560; (2) 13Co/Al₂O₃-800; (3) 13Co/MgAl₂O₄-560; (4) 13Co/MgAl₂O₄-800; (5) 13Co/SiO₂-560; (6) 13Co/SiO₂-800.

Table 1 Physicochemical properties and activity test results of supported Co-based catalysts

Sample	S_{BET}^{a} , m ² g ⁻¹	$V_{\rm p}^{\ b},{\rm cm}^3{\rm g}^{-1}$	<i>D</i> _p ^c , nm	Co _{surf} . density, atom _{Co} /nm ²	Co dispersion ^{<i>d</i>} , %	<i>D</i> _{Co} ^{<i>e</i>} , nm	$\mathrm{TOF}^{f},\mathrm{h}^{-1}$
13Co/Al ₂ O ₃ -560	146	0.25	5.7	6.7	43.6	2.3	0.4
13Co/Al ₂ O ₃ -800	130	0.25	6.5	7.5	31.2	3.1	0.7
13Co/MgAl ₂ O ₄ -560	84	0.19	7.9	11.6	28.5	3.4	1.2
13Co/MgAl ₂ O ₄ -800	73	0.19	7.9	13.4	23.4	4.2	1.9
13Co/SiO ₂ -560	225	0.86	8.7	4.3	20.3	4.3	2.5
13Co/SiO ₂ -800	168	0.73	9.6	5.8	11.5	8.5	3.9

^{*a*} Specific surface area. ^{*b*} Pore volume. ^{*c*} Pore size. ^{*d*} Co dispersion was determined by H_2 chemisorption, referred to the molar ratio of surface Co to bulk Co, with the latter being calculated from the cobalt nitrate impregnation. ^{*e*} Particle size of Co was determined by H_2 chemisorption. ^{*f*} Turn over frequency was calculated as the amount of formed isobutene per hour divided by the amount of active metal atom (determined by H_2 chemisorption) supported on catalyst after presulfidation treatment with H_2S/H_2 (30 mL min⁻¹) for 3 h at 560 °C.

intensity of diffraction peaks corresponding to CoS decreased to some extent. As for $MgAl_2O_4$ -supported catalyst, no obvious phase change was observed at high calcination temperature.

Table 1 lists the BET surface area, pore properties and Co dispersion determined by H₂ chemisorption of Co-based catalysts calcined at different temperatures. With the increase of calcination temperature, the surface area decreased noticeably for all the samples, which was indicative of the collapse of small pore walls. And this result was also consistent with the increasing trend of pore size. As for the catalysts with different supports, the surface area decreased in the following order: $13 Co/SiO_2 > 13 Co/Al_2O_3 > 13 Co/MgAl_2O_4.$ While, for the sequence of surface density of Co atom, a reverse trend to that of surface area was obtained. Furthermore, Co dispersion was determined by H₂ chemisorption, and it decreased with calcination temperature. Meanwhile, Co dispersion increased as follows: 13Co/SiO₂ < 13Co/MgAl₂O₄ < 13Co/Al₂O₃, and the calculated particle size of Co presented an opposite trend. Above results indicated that the dispersion of Co species had no direct relationship with the catalyst surface area, and the interaction between Co species and the support might play a more significant role.

3.2 Effects of support and calcination temperature

The influence of calcination temperature on dehydrogenation performance of sulfided Co-based catalysts was firstly investigated, and the results are illustrated in Fig. 2. With regard to Al₂O₃-supported catalyst, isobutane conversion decreased obviously from 76.2 wt% at 560 °C to 57.1 wt% at 800 °C. Meanwhile, the selectivity to methane and n-butane also exhibited a gradually decreasing trend, indicating that both cracking and isomerization reactions were weakened with increasing calcination temperature. Even though, the selectivity to isobutene only increased to 46.6 wt%, a relatively low level. As for 13Co/MgAl₂O₄ catalyst, the selectivity to isobutene was much higher, and it increased from 60.4 wt% to 84.0 wt% with the increase of calcination temperature. Meanwhile, isobutane conversion declined slightly at the initial stage, and then approached constant afterwards. When taking SiO₂ as the support, the selectivity to isobutene was maintained above 80 wt% at all tested calcination temperatures. However, both

isobutane conversion and isobutene selectivity decreased slightly with increasing calcination temperature. As a result, isobutene yield reduced from 61.8 wt% at 560 °C to 52.6 wt% at 800 °C. At the same time, both the selectivity to methane and *n*-butane were kept at a very low level, revealing that the sulfided 13Co/SiO₂ catalyst was almost inactive for cracking and isomerization reactions. In summary, SiO₂ seems to be the most appropriate support for Co-based catalysts in dehydrogenation.

Continuous activity test was further carried out to evaluate the stability of sulfided $13Co/SiO_2$ catalyst calcined at 560 °C, with the results shown in Fig. S1 in ESI.† Isobutane conversion decreased significantly with time on stream, especially at the initial stage, showing an obvious catalyst deactivation phenomenon. Fortunately, the decreased catalyst activity can be recovered by another sulfidation treatment. Within five continuous sulfidation-reaction cycles (see Fig. S2†), the initial isobutane conversion was maintained at a relatively steady level. To achieve continuous operation, a circulating fluidized bed unit equipped with a reactor for dehydrogenation, a regenerator for coke burning and a sulfidation section, is suggested to be employed in future industrial application.

3.2.1 Adsorption-desorption behaviors. Adsorption, surface reaction and desorption are three essential steps in heterogeneous reaction. Among these processes, adsorption and desorption behaviors significantly influence the conversion of the reactants, the prompt departure of the desired product from the catalyst, and further the catalytic performance. To obtain an ideal performance, the interaction between the reactants and catalyst surface should be properly adjusted.38 If the interaction is too strong, low steady state coverage of free sites will be formed, resulting in a low reaction rate. For the opposite case, the reactant coverage on the surface will be low, also leading to a low reaction rate. Therefore, the optimum state is an ideal coverage of adsorbed species and free sites on catalyst surface, facilitating both the adsorption of reactants and the desorption of products.

Table 2 compares the adsorption amount of isobutane and isobutene (determined by pulse experiment) over different sulfided Co-based catalysts. The adsorption amount of isobutane decreased with increasing calcination temperature, which was consistent with the decrease of isobutane conversion. Combined with the results of activity test, it can be inferred that



Fig. 2 Dehydrogenation performance of sulfided Co-based catalysts: (a and b) 13Co/Al₂O₃; (c and d) 13Co/MgAl₂O₄; (e and f) 13Co/SiO₂.

the adsorption of isobutane is not the bottleneck for isobutane dehydrogenation. As for isobutene, the adsorption amount decreased remarkably with increasing calcination temperature except for 13Co/SiO₂ catalyst. And compared with SiO₂-supported catalyst, the adsorption ability of 13Co/Al₂O₃ and 13Co/MgAl₂O₄ catalysts for isobutene was much stronger.

The transient response signals of Ar and isobutene over different sulfided Co-based catalysts during the desorption procedure are illustrated in Fig. 3. In this figure, a larger signal delay extent between Ar and isobutene indicates a harder desorption behavior of the catalysts for isobutene and a higher possibility of secondary reactions. As for sulfided catalysts with different supports, the signal delay extent decreased in the following order: $13Co/Al_2O_3 > 13Co/MgAl_2O_4 > 13Co/SiO_2$, which well explained the worst selectivity to isobutene over Al_2O_3 -supported catalysts. Moreover, with the increase of

 Table 2
 Comparison of adsorption amounts of isobutane and isobutene over sulfided Co-based catalysts calcined at different temperatures

		Adsorption amount, mL g^{-1} cat		
Sample	Calcination temperature, °C	Isobutane	Isobutene	
13Co/Al ₂ O ₃	560	0.68	2.47	
	800	0.49	1.42	
13Co/MgAl ₂ O ₄	560	0.56	1.21	
	800	0.53	0.31	
$13Co/SiO_2$	560	0.65	0.25	
	800	0.55	0.28	

calcination temperature, the signal delay extent decreased obviously over Al_2O_3 and $MgAl_2O_4$ -supported catalysts, which was consistent with the increase of selectivity to isobutene. Considering the above discussions, the desorption behaviors of the products are crucial to the selectivity.

3.2.2 Acidic and structural properties. Given the formation of a large amount of methane, propene and *n*-butane over sulfided Co-based catalysts, and the fact that the presence of acid sites is prone to affect the adsorption-desorption behaviors of the catalysts³⁹ and facilitate cracking and isomerization reactions,40-42 the acid properties of the catalysts were further determined by NH3-TPD, with the profiles demonstrated in Fig. 4. As for sulfided Co-based catalysts with different supports, both the peak temperature and the amount of NH₃ desorbed increased in the following order: 13Co/SiO₂ < 13Co/MgAl₂O₄ < 13Co/Al₂O₃, which was the same with the sequence of adsorption ability for isobutene. Such results can be explained by the fact that isobutene molecule containing a π -bond is more alkalinic than isobutane, and more likely to interact with the electron-deficient Lewis acid sites on catalyst surface.43 Therefore, the increase of acid strength and amount promoted the adsorption of isobutene, and enhanced the secondary reactions to side products.

With regard to sulfided Al_2O_3 -supported catalysts, the acidity decreased with calcination temperature, which can possibly be attributed to the consumption of Al_2O_3 for the formation of $CoAl_2O_4$ on the catalyst (as evidenced by the XRD patterns in Fig. 1). And the acid amount of MgAl_2O_4-supported catalysts also exhibited the same variation trend with increasing calcination temperature.

Based on above discussions, it can be concluded that the decrease of acid amount results in an increasing selectivity to isobutene, which is consistent with other reports.^{41,44} That is, the presence of acid sites seems to have no promoting effect on the dehydrogenation performance. However, according to Abello *et al.*,⁴³ acid sites on the catalyst facilitate the abstraction of the first hydrogen atom from C–H bond of alkane molecule, which is generally regarded as the rate-determining step. Some other researchers^{45,46} also believe that the presence of appropriate amount of acid sites facilitates the activation of alkanes. However, in this present study, the sulfided SiO₂-supported

catalysts calcined at different temperatures, almost with no acidity, exhibited a superior dehydrogenation activity and selectivity. This result indicates that the introduced sulfur also has the ability to capture the first hydrogen from isobutane molecule, and further initiates the dehydrogenation reaction. Therefore, it can be concluded that the acid sites are not necessary for this catalytic system.

According to above discussions, the support not only influences the interaction with active component but also its dispersion. As listed in Table 1, although the dispersion of Co species on SiO₂ was the worst, the sulfided Co/SiO₂ catalyst exhibited the highest TOF for isobutene formation. In contrast, alumina-supported catalysts with the best Co dispersion gave the lowest TOF value. This result suggests that Co dispersion is not the most important factor affecting the dehydrogenation performance in this catalytic system. In addition, it should also be noticed that the three evaluated supports with different acid properties, exhibited different adsorption–desorption behaviors for isobutane and isobutene and dehydrogenation performance as discussed above. From these aspects, silica, with no acidity, showed the highest prospect for application.

During catalyst preparation, the calcination temperature also influence the surface area,47-49 properties50,51 and phase composition52-55 of the catalyst remarkably. For all tested samples, the surface area decreased obviously with increasing calcination temperature, especially for silica-supported catalysts. Meanwhile, the acid amount also decreased for Al₂O₃ and MgAl₂O₄-supported catalysts, which was beneficial for obtaining a high selectivity to isobutene. In addition, the phase composition on the catalyst changed with calcination temperature. At high temperature, the interaction between Co species and the support became strong, and some solid state reactions took place. For instance, CoAl₂O₄ and Co₂SiO₄ formed on the surface of Co/Al₂O₃ and Co/SiO₂ catalysts, respectively. The generation of CoAl2O4 decreased the catalyst acidity and inhibited secondary reactions effectively. In contrast, the formation of Co₂SiO₄ (difficult to be sulfided) probably led to the decrease of active sites, and thus worsened the dehydrogenation performance.

3.3 Mechanism of different promoters

3.3.1 Sn and Cu modification. In addition to the support and calcination temperature, the effects of promoters should also be investigated. Based on our previous study,³ sulfur seems to act as a barrier to break the metal ensemble which is active for hydrogenolysis reaction, and consequently the dehydrogenation performance is improved dramatically. Accordingly, to examine if the geometric or alloy effect can inhibit hydrogenolysis reaction by isolating metal particles, different contents of Sn and Cu have been introduced into 13Co/SiO₂ catalyst in this work, and the activity test results are illustrated in Fig. 5.

To reduce the metal oxide on catalyst surface, the catalysts were prereduced by H_2 for 2 h prior to reaction. During the activity test, the following three reactions (eqn (1)–(3)) probably take place over Co-based catalysts. It can be observed in Fig. 5



Fig. 3 Transient response signals of Ar (dotted lines) and isobutene (solid lines) over different sulfided Co-based catalysts during the desorption procedure: (a) 13Co/Al₂O₃-560; (b) 13Co/Al₂O₃-800; (c) 13Co/MgAl₂O₄-560; (d) 13Co/MgAl₂O₄-800; (e) 13Co/SiO₂-560; (f) 13Co/SiO₂-800.

that, with hydrogen being supplied by deep dehydrogenation (eqn (1)) of isobutane,⁵⁶ the reduced 13Co/SiO₂ catalyst without any promoter exhibited extremely high activity for hydrogenolysis reaction and the selectivity to methane was up to 89.9 wt%.

Deep dehydrogenation: $i-C_4H_{10} \rightarrow 4C + 5H_2$ (1)

Hydrogenolysis: $i-C_4H_{10} + 3H_2 \rightarrow 4CH_4$ (2)

Dehydrogenation:
$$i-C_4H_{10} \rightarrow i-C_4H_8 + H_2$$
 (3)

After introduction of Sn and Cu, the selectivity to isobutene increased sharply with increasing Sn and Cu contents, especially for Sn-modified catalysts. When 1 wt% Sn was introduced, the selectivity to isobutene increased from 0 to 54.6 wt%, and the selectivity to methane decreased to 5.2 wt%. Such results indicated that the introduction of Sn and Cu could suppress hydrogenlysis reaction effectively. However, isobutane conversion decreased obviously at the same time, making the modification less attractive.



Fig. 4 NH₃-TPD profiles of different sulfided 13Co/support catalysts.

To study the dehydrogenation performance of Sn and Cu promoted catalysts intuitively, pulse-mode isobutane dehydrogenation was carried out with the equipment of an online MS. Taking Cu-modified catalyst for example, when no Cu was introduced, the signals of isobutane (m/z = 58) and isobutene (m/z = 56) can hardly be detected except for the first pulse (as illustrated by the MS spectra in Fig. 6a). However, the signal of methane (m/z = 16) was obvious, demonstrating that 13Co/SiO₂ catalyst exhibited extremely high hydrogenolysis activity, consistent with the results obtained by GC. After the introduction of Cu, the signal intensity of methane decreased gradually with increasing Cu content, meanwhile, that of isobutane increased obviously. In contrast, the signal intensity of isobutene increased for the initial introduction of Cu, and decreased subsequently. This observation can be attributed to the combined effects of decreasing isobutane conversion and increasing selectivity to isobutene.

As shown in Table 3, for 13Co/SiO₂ catalysts modified by Sn and Cu, Co dispersion was much larger than that over the original 13Co/SiO₂ catalyst (see Table 1), at the same time, the size of Co particles decreased obviously, indicating that the introduction of Sn or Cu destroyed the aggregated metallic species. In general, the performance of Sn or Cu promoted catalysts was similar to that of catalyst with low metal loading (*i.e.*, high selectivity to isobutene but low activity). This fact revealed that the introduction of Sn or Cu destroyed metal ensembles through geometric or alloy effect, and suppressed hydrogenolysis reaction effectively. However, the



Fig. 5 Catalytic performance of Sn or Cu promoted 13Co/SiO₂ catalyst for isobutane dehydrogenation.

6.0x10⁻⁶

4.0x10⁻⁶ m/z=16 Intensity (a.u.) 2.0x10-× 200 m/z=56 × 100 m/z=58 0.0 10 15 20 25 0 Time on stream (min) 6.0x10⁻⁶ с 4.0x10⁻⁶ Intensity (a.u.) 2.0x10-6 0.0 0 10 15 20 25 Time on stream (min) 6.0x10⁻⁶ е 4.0x10⁻⁶ Intensity (a.u.) 2.0x10⁻⁶



6.0x10

m/z=2

Fig. 6 Mass spectra of pulse-mode isobutane dehydrogenation over Cu-modified Co/SiO₂ catalysts: (a) 13Co/SiO₂; (b) 1Cu-13Co/SiO₂; (c) 2Cu-13Co/SiO₂; (d) 3Cu-13Co/SiO₂; (e) 4Cu-13Co/SiO₂; (f) 5Cu-13Co/SiO₂

dehydrogenation activity was not improved, and isobutene yield only reached to 27.5 wt% and 14.1 wt% over Sn and Cu promoted catalysts, respectively, much lower than S-modified catalyst. And the reason might lie in the difference of binding affinity between S and Sn or Cu to hydrogen atom in isobutane molecule.

Based on our previous studies,37,10 involving combined characterizations of H2-TPR, SEM, XPS and purposive activity tests, the catalytic cycle of cobalt sulfide catalyst for isobutane dehydrogenation can be speculated as Scheme 1. An isobutane

molecule adsorbs on the surface of the catalyst dissociatively, forming an intermediate with cobalt bonded to the tertiary butyl and sulfur bonded to the left hydrogen. Subsequently, the bond between β-hydrogen and sulfur weakens the C-H bond in isobutane, leading to the formation of a molecule of hydrogen. The left intermediate with a π -bonded alkene releases an isobutene molecule, meanwhile the active center is recovered. During this procedure, the high binding affinity of sulfur to two hydrogen atoms facilitates the formation of hydrogen, and the reaction equilibrium is shifted towards the right side. As a

View Article Online Paper

Table 3 Physicochemical properties of $13Co/SiO_2$ catalysts modified by different elements at calcination temperature of 560 °C

Sample	$S_{\rm BET}^{a}$,	Co _{surf} . density,	Co dispersion ^b ,	D _{Co} ^c ,
	m ² g ⁻¹	atom _{Co} /nm ²	%	nm
13Co/SiO ₂ -Sn ^d	221	4.4	34.1	2.5
13Co/SiO ₂ -Cu ^d	218	4.5	31.9	2.7
13Co/SiO ₂ -Cl ^e	230	4.2	27.1	3.2

^{*a*} Specific surface area. ^{*b*} Co dispersion was determined by H₂ chemisorption, referred to the molar ratio of surface Co to bulk Co, with the latter being calculated from the cobalt nitrate impregnation. ^{*c*} Particle size of Co was determined by H₂ chemisorption. ^{*d*} Contents of Cu and Sn in the catalyst were 5 wt%. ^{*e*} Content of Cl in the catalyst was 3.7 wt%, which was determined by XRF.



Scheme 1 Proposed catalytic cycle of sulfided Co/SiO_2 catalyst for isobutane dehydrogenation.

result, the dehydrogenation activity is improved dramatically after sulfur modification. However, as for Sn and Cu, the binding ability to hydrogen is not strong enough, therefore, the effect of Sn and Cu introduction only involves breaking metal ensembles and inhibiting hydrogenolysis reaction. **3.3.2 Cl modification.** Given a higher electronegativity than sulfur, chlorine is considered to have a stronger ability to combine with hydrogen, therefore, it has also been introduced into $13Co/SiO_2$ catalyst for the purpose of improving the dehydrogenation performance. It should be noted here that this modification was also effective in decreasing the size of Co particle size (see Table 3) and breaking the large metal ensembles into smaller ones.

Before the activity test, the catalyst sample was prereduced by hydrogen for 2 h, and then the reaction lasted for 2 h. To determine the content of chlorine on 13Co/SiO₂-Cl catalyst before and after reaction, elemental analysis was further carried out by XRF. Cl content of the fresh catalyst was 3.72 wt%, indicating that part of Cl was removed from the catalyst during the calcination process. After 2 h reaction, Cl content on the catalyst was still up to 3.58 wt%, remaining almost stable. It can be seen in Fig. 7 that, compared with 13Co/SiO₂ catalyst, the selectivity to isobutene increased remarkably after chlorine introduction, meanwhile, the selectivity to methane decreased sharply, indicating that the hydrogenolysis reaction was effectively inhibited. The decreasing catalyst activity with time on stream was probably resulted from the coke formation. Meanwhile, under the coverage and isolation effects of coke, the selectivity to isobutene increased consequently. However, isobutane conversion was constantly lower than 10 wt% for the continuous 2 h reaction. This result indicates that, although chlorine has the ability to bond with hydrogen, the introduction of chlorine could not improve the dehydrogenation activity as well. Primarily, it is worth mentioning that one chlorine atom can only bind to one hydrogen atom and can not capture βhydrogen atom at the same time. Moreover, the distance between two chlorine atoms on the catalyst surface is probably larger than that between the first hydrogen and β -hydrogen of one isobutane molecule. And even if two chlorine atoms capture the two hydrogen atoms of one isobutane simultaneously, the formation of hydrogen would still be restricted due to the untouchable distance. Therefore, the dehydrogenation activity is limited after chlorine modification.



Fig. 7 Catalytic performance of Cl promoted 13Co/SiO₂ catalyst for isobutane dehydrogenation.



Scheme 2 Schematic of promoting mechanism of different methods.

Based on the above discussions, the promoting mechanisms of different additives are summarized and depicted in Scheme 2. In general, an efficient promoter should at least satisfy the following requirements: the first is to effectively suppress the formation of metal ensembles, which are active for hydrogenolysis reaction; the second is a strong bonding affinity to hydrogen atoms; lastly, to shift the reaction equilibrium towards right side, the promoter should have the ability to combine with two hydrogen atoms simultaneously and facilitate the formation of hydrogen.

4. Conclusions

Based on the active phase of metal sulfide catalysts responsible for dehydrogenation and how they interact with isobutane molecules explored in our pervious studies, the effects of support, calcination temperature and some other promoters rather than sulfur on dehydrogenation performance of Cobased catalyst have been further investigated to optimize this novel class of catalyst in this paper.

Experimental results indicate that, both the support and calcination temperature affect Co dispersion, catalyst acid properties and the interaction between support and Co species significantly, and further influence the dehydrogenation performance. However, Co dispersion does not seem to be an important factor in this catalytic system, and the acid sites adsorb isobutene strongly and further facilitate undesired secondary reactions. As a result, silica-supported catalysts, with no acidity, exhibited the best dehydrogenation performance. But the formation of Co_2SiO_4 (hardly to be sulfided) over Co/ SiO_2 at high calcination temperatures led to an decrease of active sites and thus worsened the dehydrogenation performance. In contrast, high calcination temperature was beneficial for obtaining a high selectivity to isobutene for Al₂O₃ and MgAl₂O₄-supported catalysts.

Furthermore, detailed investigations into the effects of different additives indicate that, an efficient promoter should at least possess the following features: inhibiting the formation of metal ensembles to decrease hydrogenolysis reaction, and a strong binding affinity to two hydrogen atoms of one additive atom for enhancing dehydrogenation activity.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (no. U1362201) and the National 973 Program of China (no. 2012CB215006).

References

- 1 G. Wang, C. Li, H. Shan and W. Wu, *Ind. Eng. Chem. Res.*, 2013, 52, 13297–13304.
- 2 D. E. Resasco, B. K. Marcus, C. S. Huang and V. A. Durante, *J. Catal.*, 1994, **146**, 40–55.
- 3 G. Wang, C. Gao, X. Zhu, Y. Sun, C. Li and H. Shan, *ChemCatChem*, 2014, 6, 2305–2314.
- 4 R. W. Coughlin, A. Hasan and K. Kawakami, *J. Catal.*, 1984, **88**, 163–176.
- 5 P.-C. Liao, T. H. Fleisch and E. E. Wolf, *J. Catal.*, 1982, 75, 396–403.
- 6 M. Luo, Q. Wang, G. Li, X. Zhang, L. Wang and L. Han, *Catal. Commun.*, 2013, **35**, 6–10.
- 7 G. Wang, Z. Meng, J. Liu, C. Li and H. Shan, *ACS Catal.*, 2013, 3, 2992–3001.
- 8 G. Wang, N. Sun, C. Gao, X. Zhu, Y. Sun, C. Li and H. Shan, *Appl. Catal., A*, 2014, **478**, 71–80.
- 9 Y.-n. Sun, L. Tao, T. You, C. Li and H. Shan, *Chem. Eng. J.*, 2014, **244**, 145–151.
- 10 G. Wang, C. Li and H. Shan, ACS Catal., 2014, 1139-1143.
- 11 M. Chen, J. L. Wu, Y. M. Liu, Y. Cao, L. Guo, H. Y. He and K. N. Fan, *Appl. Catal.*, *A*, 2011, **407**, 20–28.
- 12 R. Grabowski, Catal. Rev.: Sci. Eng., 2006, 48, 199-268.
- 13 M. Bhasin, J. McCain, B. Vora, T. Imai and P. Pujado, *Appl. Catal.*, *A*, 2001, **221**, 397–419.
- 14 F. Hoxha, B. Schimmoeller, Z. Cakl, A. Urakawa, T. Mallat, S. E. Pratsinis and A. Baiker, *J. Catal.*, 2010, **271**, 115–124.
- E. Schmidt, F. Hoxha, T. Mallat and A. Baiker, *J. Catal.*, 2010, 274, 117–120.
- 16 C. Chen, J. Cao, M. Cargnello, P. Fornasiero and R. J. Gorte, J. Catal., 2013, 306, 109–115.
- 17 A. M. Abdel-Mageed, S. Eckle, H. G. Anfang and R. J. Behm, *J. Catal.*, 2013, **298**, 148–160.
- 18 K. Lv, Q. Xiang and J. Yu, Appl. Catal., B, 2011, 104, 275-281.

- 19 L. Ma, J. Li, H. Arandiyan, W. Shi, C. Liu and L. Fu, *Catal. Today*, 2012, **184**, 145–152.
- Z. Boukha, L. Fitian, M. López-Haro, M. Mora, J. R. Ruiz,
 C. Jiménez-Sanchidrián, G. Blanco, J. J. Calvino,
 G. A. Cifredo and S. Trasobares, *J. Catal.*, 2010, 272, 121–130.
- 21 D. Duvenhage and N. Coville, *Appl. Catal., A*, 2002, **233**, 63–75.
- 22 V. Ravat, I. Nongwe, R. Meijboom, G. Bepete and N. J. Coville, *J. Catal.*, 2013, **305**, 36–45.
- 23 F. B. Passos, M. Schmal and M. A. Vannice, J. Catal., 1996, 160, 106–117.
- 24 F. B. Passos, D. A. G. Aranda and M. Schmal, *J. Catal.*, 1998, **178**, 478–488.
- 25 J. Z. Zhang, Y.-T. Tsai, K. L. Sangkaewwattana and J. G. Goodwin Jr, *J. Catal.*, 2011, **280**, 89–95.
- 26 G. S. Ranhotra, A. T. Bell and J. A. Reimer, *J. Catal.*, 1987, **108**, 40–49.
- 27 R. J. Lobo-Lapidus and B. C. Gates, *J. Catal.*, 2009, **268**, 89–99.
- 28 C. R. Apesteguía and J. Barbier, J. Catal., 1982, 78, 352-359.
- 29 J. C. Serrano-Ruiz, A. Sepúlveda-Escribano and F. Rodríguez-Reinoso, J. Catal., 2007, 246, 158–165.
- 30 R. D. Cortright and J. A. Dumesic, *J. Catal.*, 1994, **148**, 771–778.
- 31 M. C. Román-Martínez, J. A. Maciá-Agulló, I. M. J. Vilella, D. Cazorla-Amorós and H. Yamashita, *J. Phys. Chem. C*, 2007, **111**, 4710–4716.
- 32 X. Wang, L. Altmann, J. Stöver, V. Zielasek, M. Bäumer, K. Al-Shamery, H. Borchert, J. Parisi and J. Kolny-Olesiak, *Chem. Mater.*, 2012, 25, 1400–1407.
- 33 J. H. Sinfelt, J. Carter and D. Yates, *J. Catal.*, 1972, **24**, 283–296.
- 34 G. A. Martin and J. A. Dalmon, J. Catal., 1982, 75, 233-242.
- 35 K. Lu and B. J. Tatarchuk, J. Catal., 1987, 106, 166-175.
- 36 K. Lu and B. J. Tatarchuk, J. Catal., 1987, 106, 176-187.
- 37 E. T. Iyagba, T. Eddy Hoost, J. U. Nwalor and J. G. Goodwin Jr, J. Catal., 1990, 123, 1–11.
- 38 B. Yang, R. Burch, C. Hardacre, G. Headdock and P. Hu, ACS Catal., 2013, 4, 182–186.

- 39 R. Grabowski, B. Grzybowska, K. Samson, J. Słoczyński, J. Stoch and K. Wcisło, *Appl. Catal.*, A, 1995, 125, 129–144.
- 40 K. Chen, S. Xie, E. Iglesia and A. T. Bell, *J. Catal.*, 2000, **189**, 421–430.
- 41 L. Madeira, M. Portela, C. Mazzocchia, A. Kaddouri and R. Anouchinsky, *Catal. Today*, 1998, **40**, 229–243.
- 42 S. Ge, C. Liu and L. Wang, Chem. Eng. J., 2001, 84, 497-502.
- 43 M. Abello, M. Gomez and O. Ferretti, *Appl. Catal.*, A, 2001, 207, 421–431.
- 44 K. Chen, A. T. Bell and E. Iglesia, *J. Phys. Chem. B*, 2000, **104**, 1292–1299.
- 45 J. C. Vedrine, J. M. M. Millet and J.-C. Volta, *Catal. Today*, 1996, **32**, 115–123.
- 46 A. Pantazidis, A. Auroux, J. M. Herrmann and C. Mirodatos, *Catal. Today*, 1996, **32**, 81–88.
- 47 V. R. Choudhary, D. K. Dumbre, N. S. Patil, B. S. Uphade and S. K. Bhargava, *J. Catal.*, 2013, **300**, 217–224.
- 48 E. Aneggi, N. J. Divins, C. de Leitenburg, J. Llorca and A. Trovarelli, *J. Catal.*, 2014, **312**, 191–194.
- 49 C. Kang, L. Jing, T. Guo, H. Cui, J. Zhou and H. Fu, *J. Phys. Chem. C*, 2008, **113**, 1006–1013.
- 50 H. Yamashita, Y. Horiuchi, S. Imaoka, S. Nishio, N. Nishiyama and K. Mori, *Catal. Today*, 2008, **132**, 146–152.
- 51 P. Górska, A. Zaleska, E. Kowalska, T. Klimczuk, J. W. Sobczak, E. Skwarek, W. Janusz and J. Hupka, *Appl. Catal.*, *B*, 2008, 84, 440–447.
- 52 F. Liu, K. Asakura, H. He, Y. Liu, W. Shan, X. Shi and C. Zhang, *Catal. Today*, 2011, **164**, 520–527.
- 53 D. Y. Yoon, J.-H. Park, H.-C. Kang, P. S. Kim, I.-S. Nam, G. K. Yeo, J. K. Kil and M.-S. Cha, *Appl. Catal.*, *B*, 2011, 101, 275–282.
- 54 K. Li, H. Wang, Y. Wei and D. Yan, *Int. J. Hydrogen Energy*, 2011, **36**, 3471–3482.
- 55 X. Guo, D. Mao, G. Lu, S. Wang and G. Wu, *Catal. Commun.*, 2011, **12**, 1095–1098.
- 56 E. A. Redekop, V. V. Galvita, H. Poelman, V. Bliznuk,
 C. Detavernier and G. B. Marin, ACS Catal., 2014, 4, 1812– 1824.